

COLLECTIVE SURFACE DIFFUSION NEAR A FIRST-ORDER PHASE TRANSITION

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ABSTRACT. For a large class of lattice models we study the thermodynamic factor, Φ , of the collective surface diffusion coefficient near a first-order phase transition between two phases at low temperatures. In a two-phase regime its dependence on the coverage, θ , is $\Phi \approx \theta / [(\theta - \theta_-)(\theta_+ - \theta)N]$, where N is the number of adsorption sites and θ_{\pm} are the single-phase coverages at the transition. In the crossover between the two-phase and single-phase regimes $\Phi(\theta)$ is shown to have a more complex behavior. The results are applied to a simple 2D lattice model.

Surface diffusion is an intriguing phenomenon that has attracted much attention of surface scientists in the past few decades [1, 2]. One of the relevant transport coefficients for surface diffusion is the collective (or chemical) surface diffusion coefficient, D_c . It is associated with the decay of fluctuations in the adparticle density at large time and space intervals and is defined via the Fick's first law, $\mathbf{J} = -D_c \nabla \theta$, where \mathbf{J} is the surface diffusion flux and θ is the surface coverage.

Considering suitable 2D lattice gas models, computer simulation methods have been frequently applied in theoretical studies of D_c (and of surface diffusion in general) with a particular interest in the presence of phase transitions and their effects on surface diffusion [3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Usually, the observation that $D_c = \Phi D_{CM}$ [1] was used, where D_{CM} is the center of mass diffusion coefficient and represents kinetic properties of D_c , while $\Phi = \langle N_{oc} \rangle / (\langle N_{oc}^2 \rangle - \langle N_{oc} \rangle^2)$ is associated with thermodynamic properties of D_c and is called the thermodynamic factor (N_{oc} is the number of adsorption sites in a system occupied by adparticles and $\langle \cdot \rangle$ denotes the statistical mean value). The factor is simply related to the coverage $\theta = \langle N_{oc} \rangle / N$ and isothermal susceptibility $\chi = \beta(\langle N_{oc}^2 \rangle - \langle N_{oc} \rangle^2)/N$,

$$\Phi = \beta \frac{\theta}{\chi}, \quad (1)$$

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where N is the total number of adsorption sites in the system and $\beta = 1/k_B T$ is the inverse temperature. In the hydrodynamic limit (when θ varies slowly with space and time) D_c can be obtained from the system free energy, and so it is a purely thermodynamic quantity [13, 14, 15].

In this letter we use a rigorous statistical mechanical approach to study Φ near a first-order phase transition with a (in general asymmetric) coexistence of two phases (denoted as ‘+’ and ‘−’). To this end, we consider a finite array of N adsorption sites with periodic boundary conditions and use that, for a wide range of classical lattice spin models (such as the models with a finite range m -potential and a finite number of ground states), the coverage and susceptibility in the array have a remarkably universal behavior near such a transition [16, 17]. Hence, the behavior of Φ near the transition as a function of the chemical potential, μ , as well as of the coverage θ can be described in a very general and unifying way. It is only needed that the temperature is low (β is large) and that the array is large and not too oblong (N is large and the number of boundary sites in the array is of order of a fractional power of N).

The μ -dependence of Φ near the transition. Generally, the coverage can be expressed as [16]

$$\theta = (-f'_+) \lambda_+ + (-f'_-) \lambda_- + R_N, \quad (2)$$

where f_{\pm} and $-f'_{\pm}$ are single-phase specific free energies and coverages, respectively, the weight factors $\lambda_{\pm} = 1/\{1 + \exp[\pm\beta(f_+ - f_-)N]\}$, and the error term $R_N = O(\exp(-c\beta\sqrt{N}))$ with $c > 0$ (primes denote derivatives with respect to μ , and $O(x)$ stands for a term that can be bounded by const x). To get an explicit μ -dependence of θ near a transition point, μ_t , one applies Taylor expansions around μ_t , yielding [16]

$$\theta = \frac{\vartheta_0}{2} + \frac{\Delta\vartheta}{2} \tanh \frac{Y}{2} + O(\beta^2|\mu - \mu_t|^2) + R_N \quad (3)$$

(see Fig. 1(a)). The shorthands $q_0 = q_+ + q_-$ and $\Delta q = q_+ - q_-$ denote the sum and difference, respectively, of any single-phase quantities q_{\pm} , $\vartheta_{\pm} = \theta_{\pm} + \chi_{\pm}(\mu - \mu_t)$, and $Y = \beta N(\mu - \mu_t)[\Delta\theta + \Delta\chi(\mu - \mu_t)/2]$, where $\theta_{\pm} = -f'_{\pm}(\mu_t)$ and $\chi_{\pm} = -f''_{\pm}(\mu_t)$ are the single-phase coverages and susceptibilities at the transition. If the plus (minus) corresponds to the phase stable above (below) μ_t , the coverage jump at μ_t is $\theta(\mu_t + 0) - \theta(\mu_t - 0) = \Delta\theta > 0$. For μ beyond the transition Eq. (2) yields another expression for θ [16],

$$\theta = \theta_{\infty} + P_N + R_N. \quad (4)$$

The infinite-volume coverage θ_∞ is equal to $-f'_+$ ($-f'_-$) for μ above (below) μ_t and $P_N = O(\exp(-C|\mu - \mu_t|\beta N))$ with $C > 0$. Using $s = \text{sign}(\mu - \mu_t)$ both for numbers ± 1 and for subscripts ‘ \pm ’, we may write $\theta_\infty = -f'_s$.

Equation (2) holds also for the μ -derivatives of θ with the same error term R_N [16]. So, we can readily obtain a general expression for the susceptibility,

$$\chi = (-\Delta f')^2 \beta N \lambda_+ \lambda_- + (-f''_+) \lambda_+ + (-f''_-) \lambda_- + R_N, \quad (5)$$

where $-f''_\pm$ are the single-phase susceptibilities. The μ -dependence of χ then follows analogously to that of θ : either from Taylor expansions around μ_t (useful near the transition),

$$\chi = \frac{\Delta \vartheta^2 \beta N}{4 \cosh^2 \frac{Y}{2}} + \frac{\chi_0}{2} + \frac{\Delta \chi}{2} \tanh \frac{Y_1}{2} \quad (6)$$

$$+ O(\beta^3 N |\mu - \mu_t|^2) + O(\beta^2 |\mu - \mu_t|) + R_N \quad (7)$$

with $Y_1 = \Delta \theta \beta N (\mu - \mu_t)$ (see Fig. 1(b)), or by using the infinite-volume susceptibility $\chi_\infty = -f''_s$ (useful beyond the transition),

$$\chi = \chi_\infty + O(\beta N P_N) + R_N. \quad (8)$$

These formulas for θ and χ immediately yield the μ -dependence of the thermodynamic factor Φ . Near the transition region, $|\mu - \mu_t| \ll 1$, it is given by Eqs. (3) and (6) (see Fig. 1(c)), while farther away from the transition, $|\mu - \mu_t| \gg 1/N$, it is given by Eqs. (4) and (8).

At a certain distance from μ_t (both below and above μ_t) there are two narrow regions of μ where θ and χ reduce to their infinite-volume limits θ_∞ and χ_∞ so that the behavior of Φ switches from a two-phase regime to one of the two single-phase regimes (see Fig. 1(c)). According to Eqs. (3) and (6), these two crossover regions occur when $\beta N \exp(-|Y|)$ becomes small, i.e., within the intervals $\delta \mu_- \leq |\mu - \mu_t| \leq \delta \mu_+$, where $\delta \mu_\pm = (\ln N \pm K \ln \ln N) / \Delta \theta \beta N$ with $K > 0$ large.

The θ -dependence of Φ near the transition. The coverage dependence of Φ follows upon the elimination of μ between $\theta(\mu)$ and $\chi(\mu)$. This procedure is simple to achieve within the two-phase regime, $|\mu - \mu_t| \leq \delta \mu_-$, because it reduces to the elimination of Y between Eqs. (3) and (6). We readily get

$$\Phi = \frac{\theta}{(\theta - \theta_-)(\theta_+ - \theta)N + O(\ln N)}, \quad t_- \leq \theta \leq t_+, \quad (9)$$

where $t_\pm = \theta(\mu_t \pm \delta \mu_-)$ are the most extreme values that θ attains in the two-phase regime. Since $t_\pm = \theta_\pm \mp \Delta \theta \ln^K N / N + O(\ln N / N)$ by

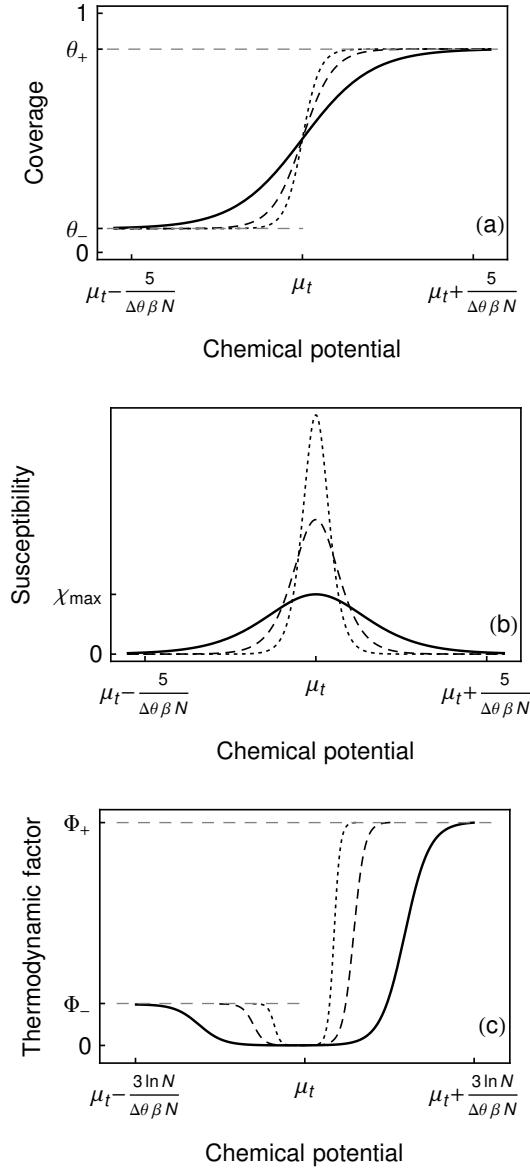


FIGURE 1. The dependencies of (a) coverage, (b) susceptibility, and (c) thermodynamic factor on the chemical potential near the transition (full lines). For two larger sizes of a system the dependencies are depicted by dashed and dotted curves. The points $\chi_{\max} \approx (\Delta\theta/2)^2\beta N$ and $\Phi_{\pm} \approx \beta\theta/\chi_{\pm}$.

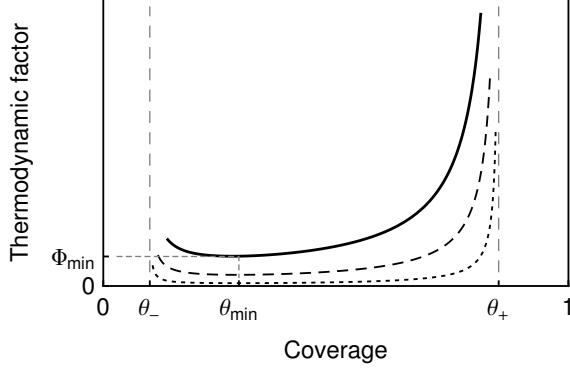


FIGURE 2. The θ -dependence of Φ (the full line) in the interval $t_- \leq \theta \leq t_+$ (the two-phase regime) as given by Eq. (9). For two larger sizes of a system the dependence is depicted by a dashed and a dotted curve. A minimum of Φ is attained at $\theta_{\min} \approx (\theta_- - \theta_+)^{1/2}$ and its value is $\Phi_{\min} \approx 1/(\sqrt{\theta_-} - \sqrt{\theta_+})^2 N$.

Eq. (3), we have $\theta_- < t_- < t_+ < \theta_+$. The behavior of Φ as given by Eq. (9) is shown in Fig. 2.

Next, consider the range $\delta\mu_- \leq |\mu - \mu_t| \leq d\mu$ with $d\mu = 1/\Delta\theta\beta N^{3/4}$ that contains both crossover regions as well as a part of either single-phase regime (instead of $N^{3/4}$ any power N^α with $1/2 < \alpha < 1$ can be considered). To eliminate μ between $\theta(\mu)$ and $\chi(\mu)$ we rewrite Eqs. (3) and (6) as $\theta = \theta_s + s\chi_s|\mu - \mu_t| - s\Delta\theta A + Q_N$ and $\chi = \Delta\theta^2\beta N A + \chi_s + \beta N Q_N$, respectively, with $A = \exp(-|Y_1|)$ and $Q_N = O(\ln^K N/N^{3/2})$. Eliminating A between these equations, we get

$$\Phi = \begin{cases} \frac{\theta}{\frac{\chi_-}{\beta}(\omega_-+1)+O(NQ_N)}, & \tau_- \leq \theta \leq t_-, \\ \frac{\theta}{\frac{\chi_+}{\beta}(\omega_++1)+O(NQ_N)}, & t_+ \leq \theta \leq \tau_+, \end{cases} \quad (10)$$

with

$$\omega_\pm = W\left(\frac{\Delta\theta^2\beta N}{\chi_\pm} \exp\left[\pm\frac{\Delta\theta\beta N}{\chi_\pm}(\theta_\pm - \theta)\right]\right),$$

where $W(y)$ is the Lambert W -function (i.e., the inverse to $y = W \exp W$) and the restrictions on θ in Eq. (10) correspond to the two intervals of values attained by θ in the considered μ -region below and above μ_t . Thus, $\tau_\pm = \theta(\mu_t \pm d\mu) = \theta_\pm \pm \chi_\pm/\Delta\theta\beta N^{3/4} + O(1/N^{3/2})$ by Eq. (3) so that $\tau_- < \theta_- < t_- < t_+ < \theta_+ < \tau_+$.

The behavior of Φ as given by Eq. (10) is shown in Fig. 3. If $\omega_\pm \gg 1$, the two-phase behavior of Φ prevails, while a single-phase

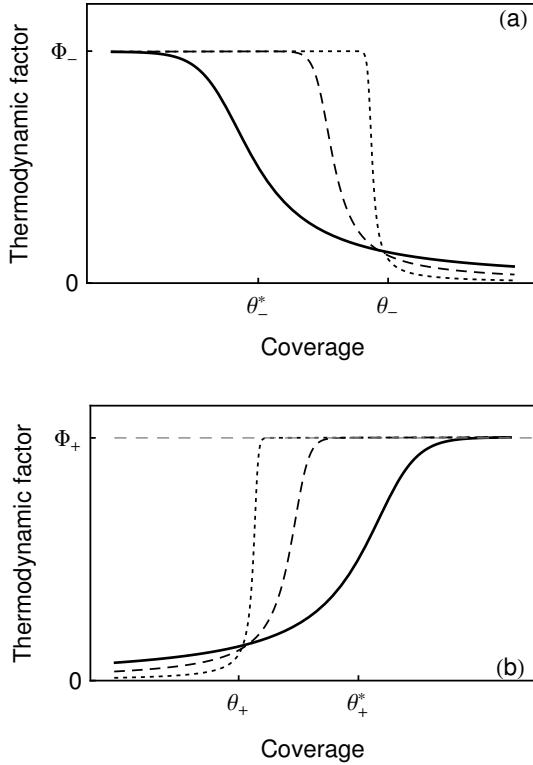


FIGURE 3. The θ -dependence of Φ (full lines) in the crossover regions (a) near θ_- and (b) near θ_+ as given by Eq. (10) (the error term $O(NQ_N)$ is neglected). For two larger sizes of a system the dependencies are depicted by dashed and dotted curves.

behavior is dominant for $\omega_{\pm} \ll 1$. The crossover occurs when ω_{\pm} is comparable to 1, i.e., when θ is comparable to the value, $\theta_{\pm}^* = \theta_{\pm} \pm (\chi_{\pm}/\Delta\theta\beta N) [\ln(\Delta\theta^2\beta N/\chi_{\pm}) - 1]$, at which $\omega_{\pm} = 1$. For $\theta \lesssim \theta_-^*$ (for $\theta \gtrsim \theta_+^*$) the thermodynamic factor is increasing in approximately a linear way as $\beta\theta/\chi_-$ (as $\beta\theta/\chi_+$), while as θ crosses θ_-^* (θ_+^*) and gets above θ_- (below θ_+) it approaches the two-phase behavior described by Eq. (9).

An example. To illustrate the above results, we consider the following one-component lattice-gas model of diffusion on a triangular lattice [3, 5, 6]. Each lattice site is either occupied by an adparticle or is vacant. The model Hamiltonian is $H = \varepsilon N_{\text{oc}}^b - \mu N_{\text{oc}}$, where N_{oc}^b is the number of nearest-neighbor bonds occupied by adparticles and $\varepsilon < 0$ is an attractive interaction between two closest adparticles. The model is

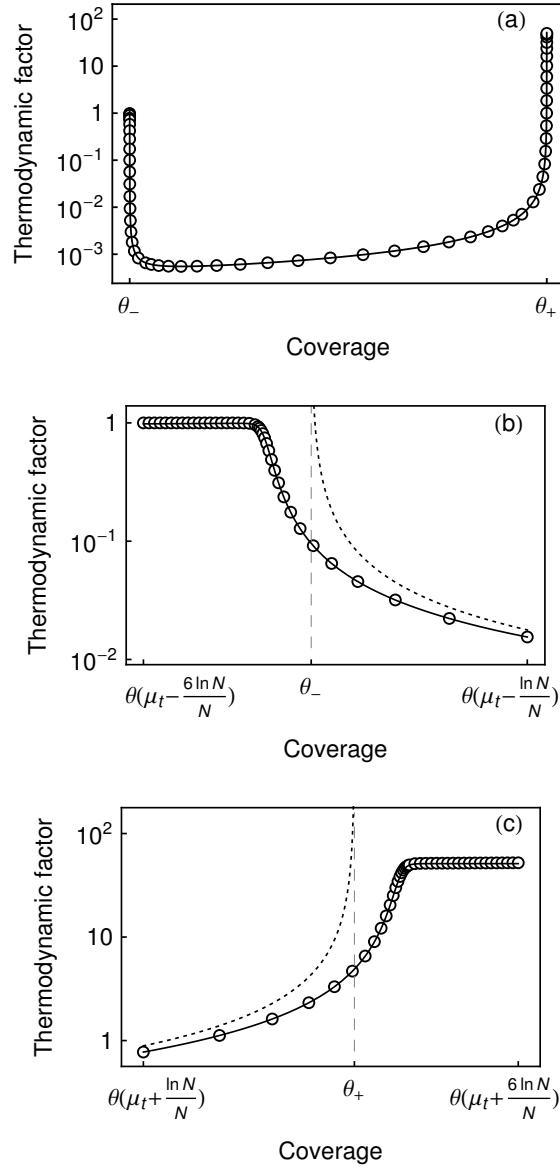


FIGURE 4. The θ -dependence of Φ for the example model with $N = 50 \times 50$ and $\beta|\varepsilon| = 1.2 \ln 3$ in (a) the two-phase regime, (b) the crossover region below μ_t , and (c) the crossover region above μ_t . Circles are values of Φ obtained numerically upon elimination of μ between $\theta(\mu)$ and $\chi(\mu)$ using Eqs. (2) and (5). Full lines correspond to formulas (9) (case (a)) and (10) (cases (b) and (c)). Dotted lines in (b) and (c) correspond to the two-phase regime formula (9).

equivalent to the standard Ising model, and at low temperatures (for $\beta|\varepsilon| > \ln 3$) it exhibits a first-order phase transition at $\mu_t = 3\varepsilon$ between a fully vacant phase (stable below μ_t and thus corresponding to $-$) and a fully occupied phase (stable above μ_t and corresponding to $+$) [18].

As follows from Ref. [16], one has $f_{\pm} = e_{\pm} + s_{\pm}$, where $e_+ = 3\varepsilon - \mu$ and $e_- = 0$ are the specific ground state energies and s_{\pm} represent thermal excitations over the ground states and can be expressed by cluster expansions. In the lowest order approximation $s_{\pm} \approx -\exp(-\beta\Delta H_{\pm})/\beta$, where $\Delta H_+ = \mu - 6\varepsilon$ and $\Delta H_- = -\mu$ are the energy excesses of the lowest excited states (one adparticle taken from and added to the corresponding ground state). So, $-f'_+ \approx 1 - \eta \exp[-\beta(\mu - \mu_t)]$, $-f'_- \approx \eta \exp[\beta(\mu - \mu_t)]$, and $-f''_{\pm} \approx \beta\eta \exp[\mp\beta(\mu - \mu_t)]$ with $\eta = \exp(\beta\mu_t)$. The thermodynamic factor Φ of the model can be readily obtained from these expressions and Eqs. (2) and (5), and it is shown in Fig. 4. Moreover, in the single-phase regimes, $|\mu - \mu_t| \geq d\mu$, Eqs. (4) and (8) yield $\Phi \approx 1 + O(NP_N)$ for μ below μ_t (i.e., for θ near 0) and $\Phi \approx \theta/(1-\theta) + O(NP_N)$ for μ above μ_t (i.e., θ near 1). Thus, $D_c \approx D_{CM}$ at low coverages, while the Langmuir relation holds at high coverages.

Finally, $D_c = D_c^0 \beta \exp(\beta\mu) P_{00}/\chi$ in the hydrodynamic limit [5], where D_c^0 is the diffusion coefficient of non-interacting adparticles and $P_{00} = 1 - 2\theta + (\partial f/\partial\varepsilon)/3$ is the probability that two nearest-neighbor sites are empty ($f = -k_B T \ln Z/N$ is the system specific free energy). Using the results of Ref. [16], we get $\partial f/\partial\varepsilon = [(\partial f_+/\partial\varepsilon)\lambda_+ + (\partial f_-/\partial\varepsilon)\lambda_-](1 + R_N)$. Along with the above formulas, we find that at $\mu = \mu_t$, say, one has $\ln(D_c/D_c^0) \approx -3|\varepsilon|/k_B T - \ln[(1 - 2\eta)^2 N/2] + O(1/N)$.

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